Voyages on the Atlantic – A Study of Oceanic Alkyl Nitrates

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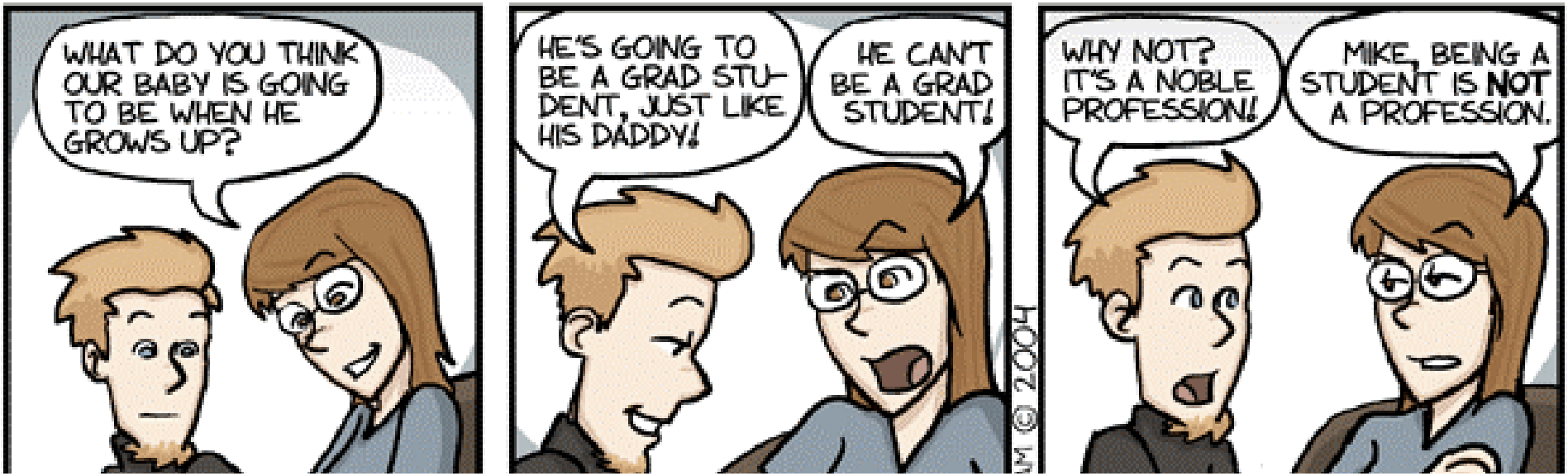
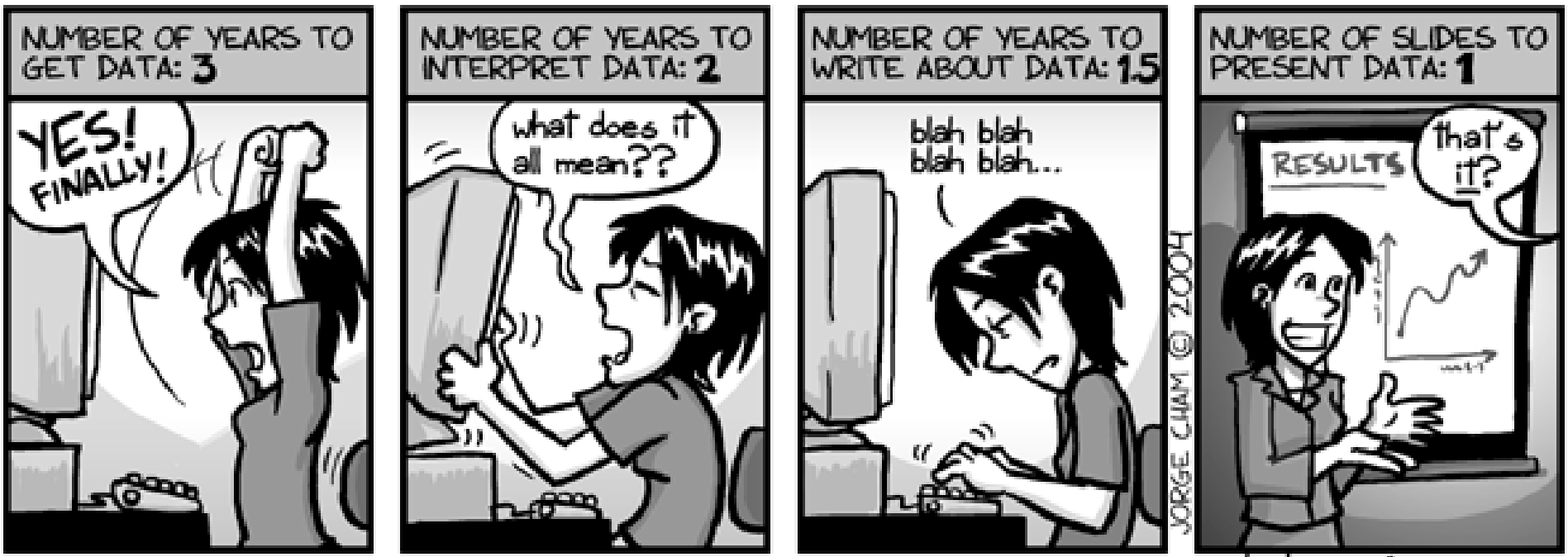
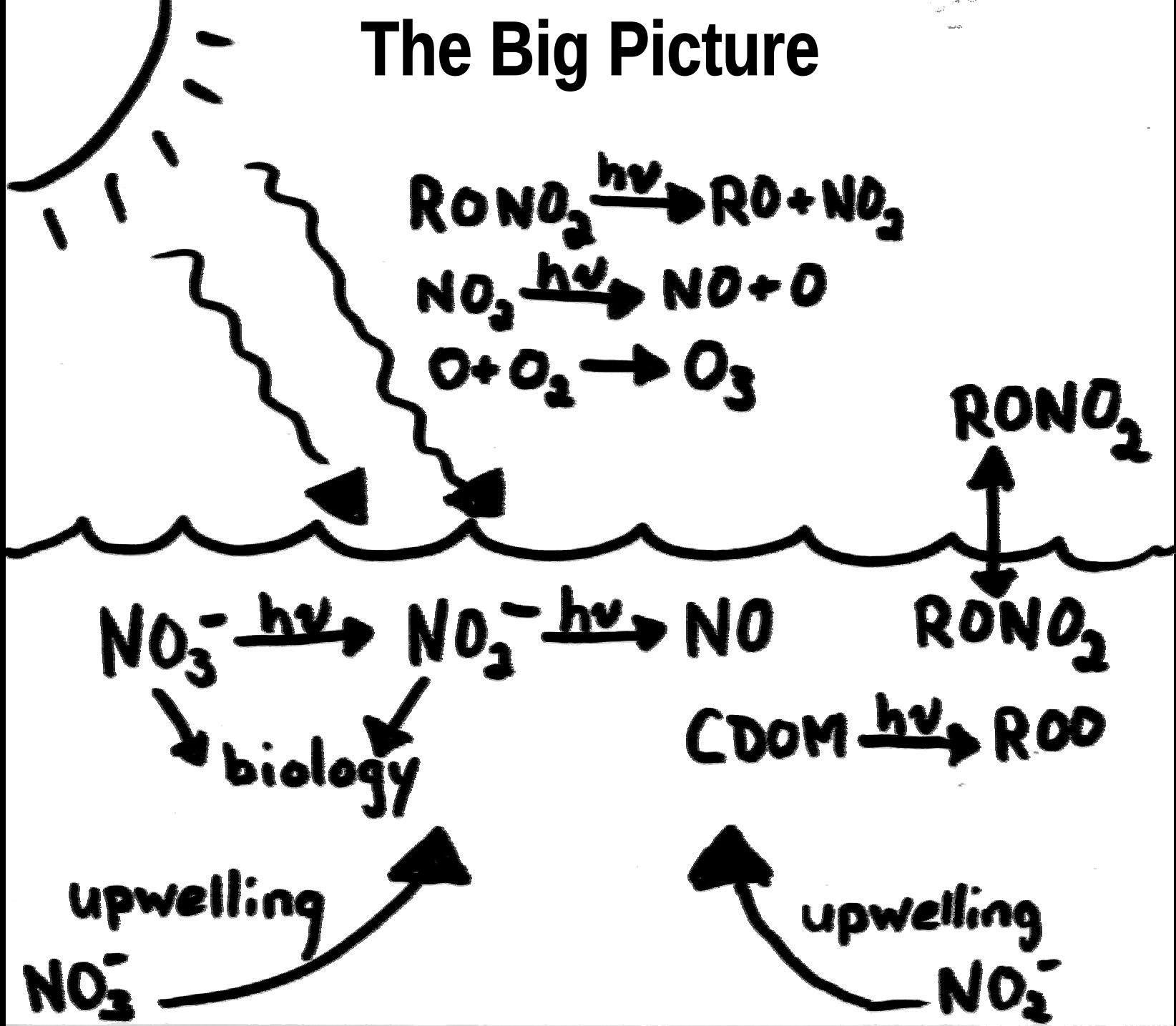


DATA: BY THE NUMBERS



The Big Picture



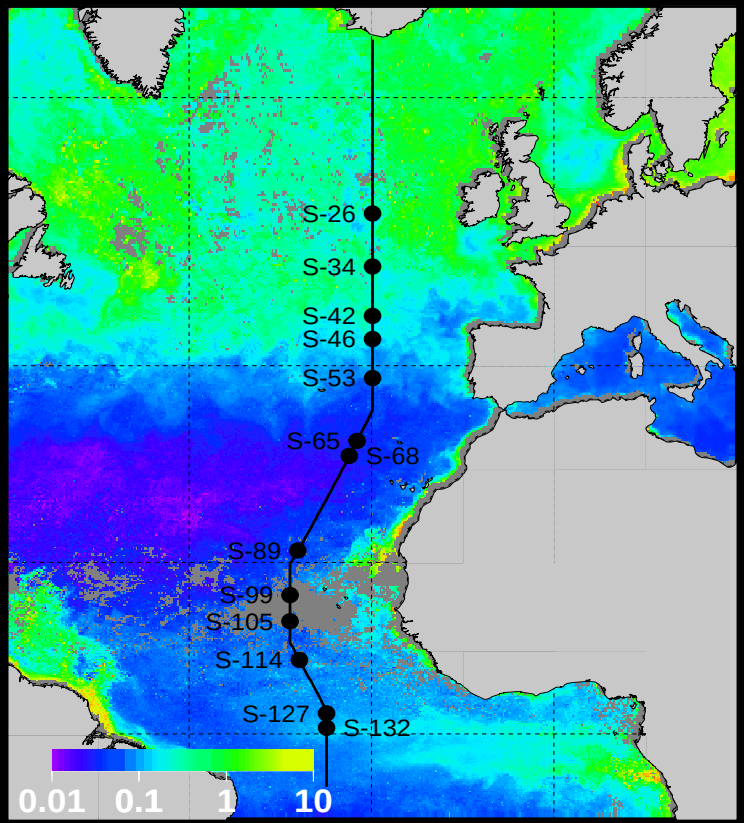
Reaction Mechanism

$$NO_2^- \xrightarrow{h\nu,\ H_2O} NO + OH + OH^-$$

$$CDOM \xrightarrow{h\nu \text{ or } OH} ROO^{\cdot}$$

$$ROO^{\cdot} + NO \rightarrow RO + NO_2 \text{ or } RONO_2$$

The Cruise Track



- June 19 – Left Reykjavik Iceland
- July 10 – Arrived Funchal, Madeira
- July 15 – Left Madeira
- August 11 – Arrived in Natal, Brazil

The Ship – Ronald H. Brown

Goals of Study

- Measure depth profiles of C1-C3 alkyl nitrates.
- Incubation experiments to determine production rates of alkyl nitrates under ‘natural’ conditions.

How is Deep Water Sampled?

- Conductivity-Temperature-Depth (CTD) Rosette
- 35 bottles

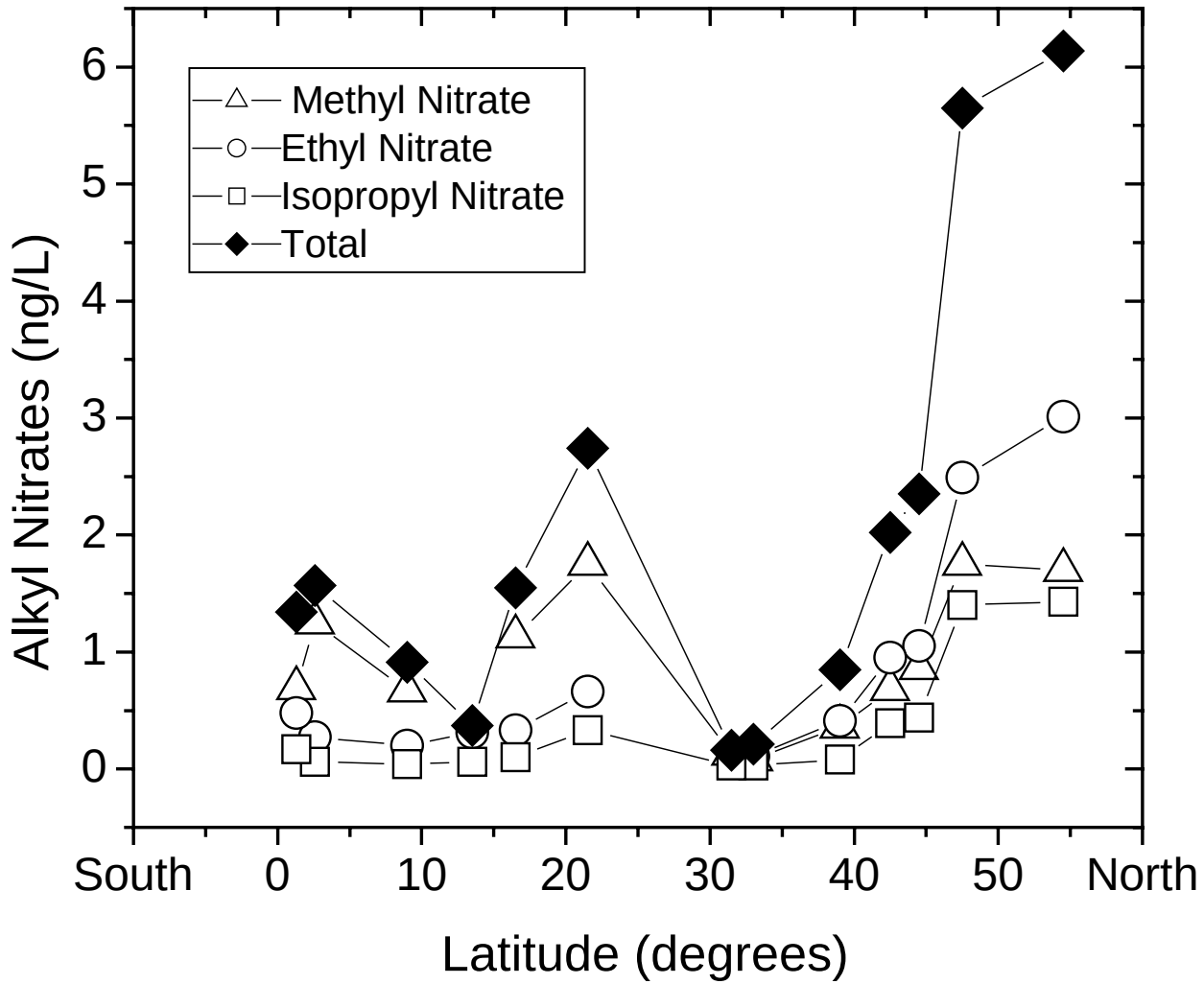
Sampling Water for Gas Measurements

- Glass syringes
- Important to avoid bubbles.

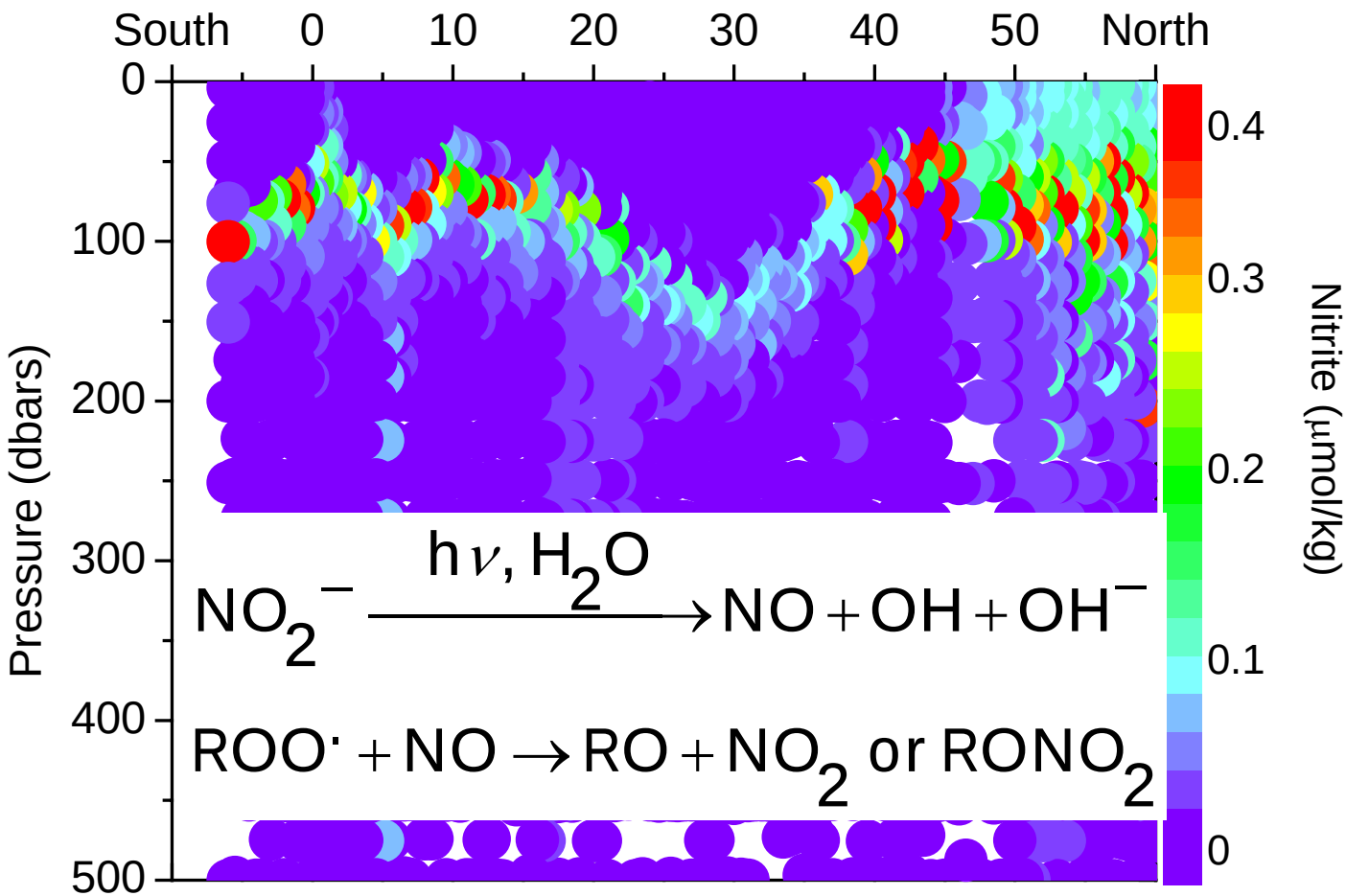
Alkyl Nitrate Detection

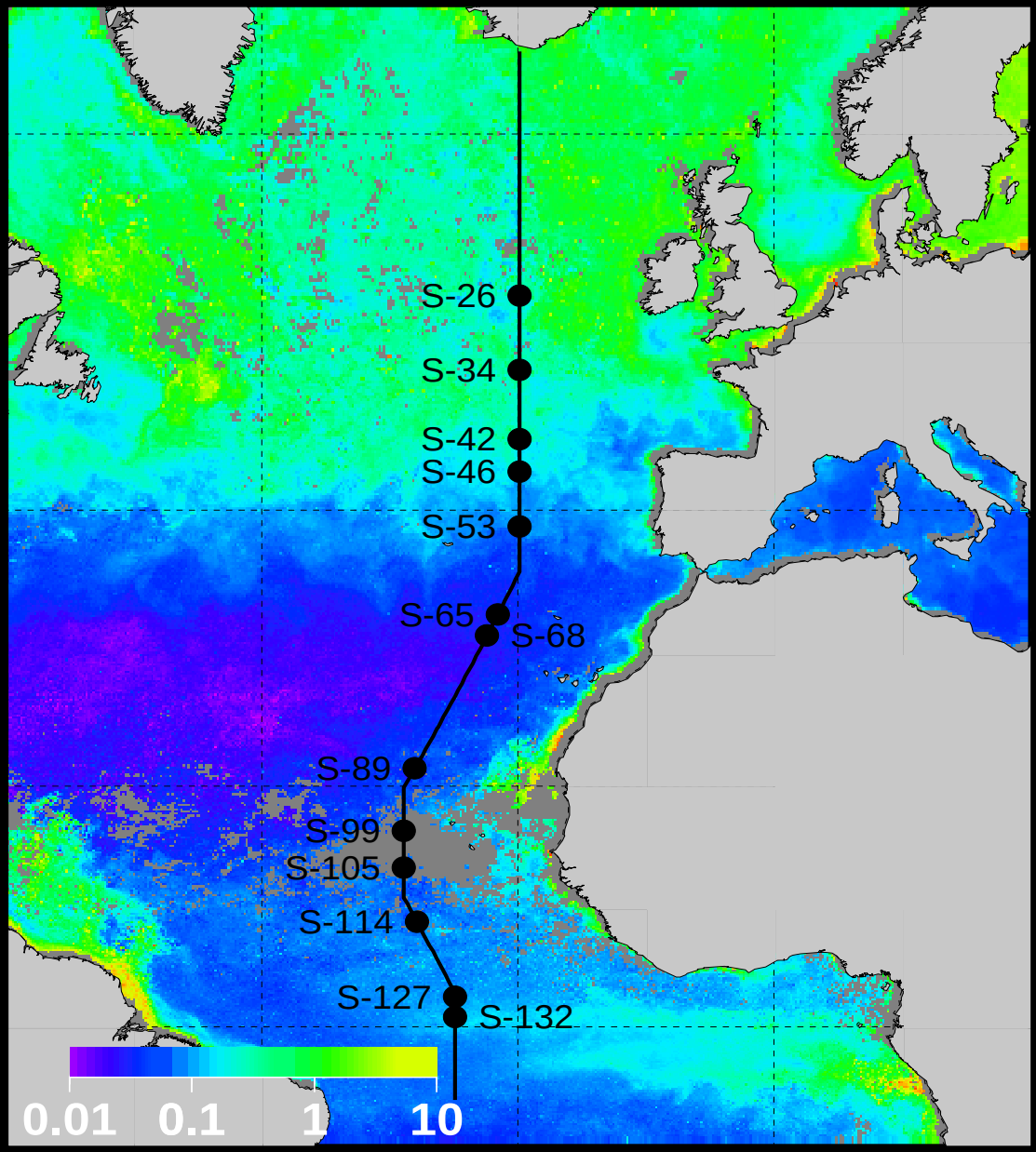
- Purge and trap
- Trap on stainless steel w/liquid nitrogen
- Gas chromatograph for separation
- Quadrapole mass spectrometer to analyze

Surface Ocean Alkyl Nitrates



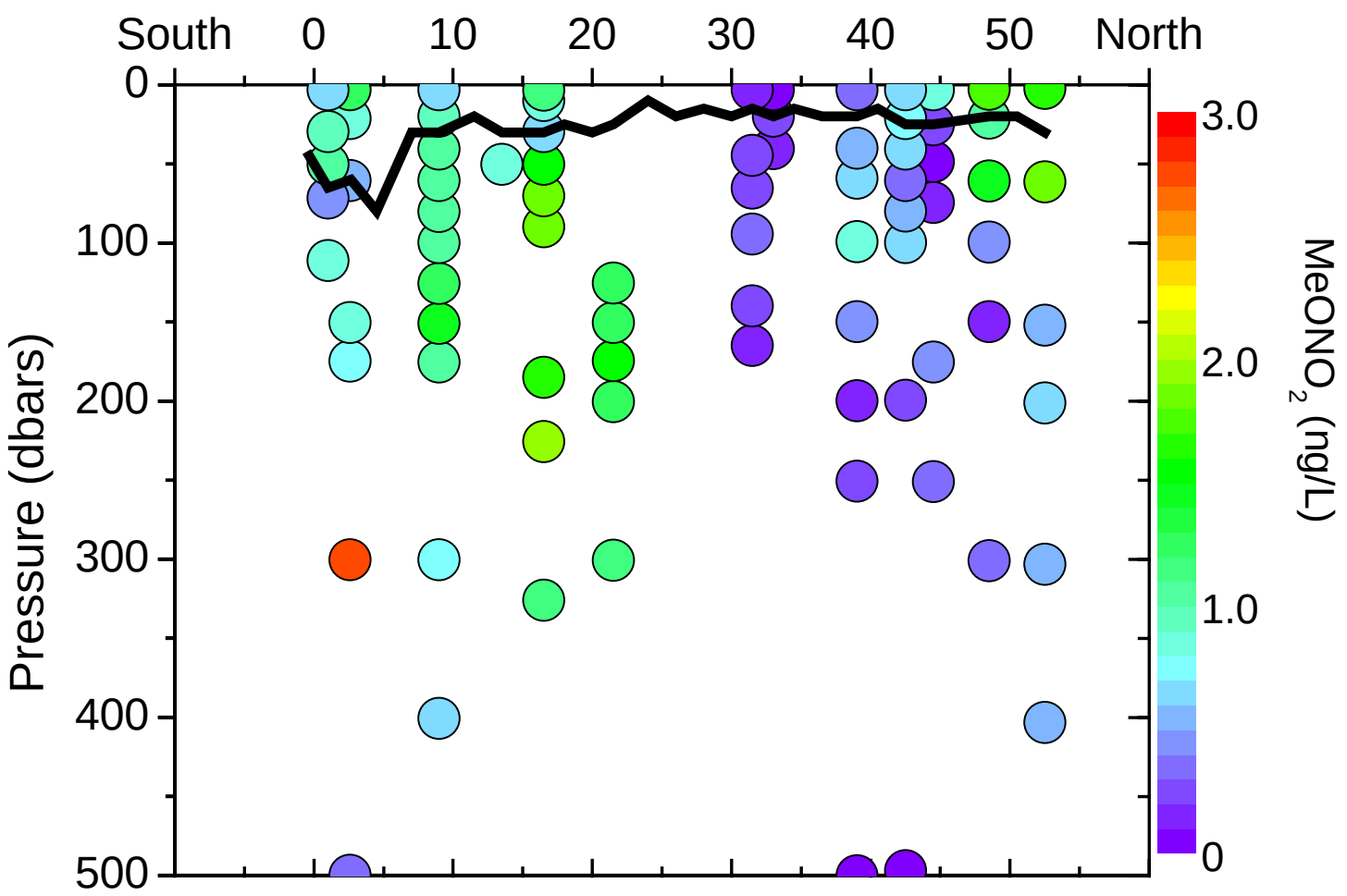
Nitrite


South
0
10
20
30
40
50
North
Pressure (dbars)
0
100
200
300
400
500
0.4
0.3
0.2
0.1
0
Nitrite (µmol/kg)
$NO_2^- \xrightarrow{h\nu, H_2O} NO + OH + OH^-$
$ROO^{\cdot} + NO \rightarrow RO + NO_2$ or $RONO_2$

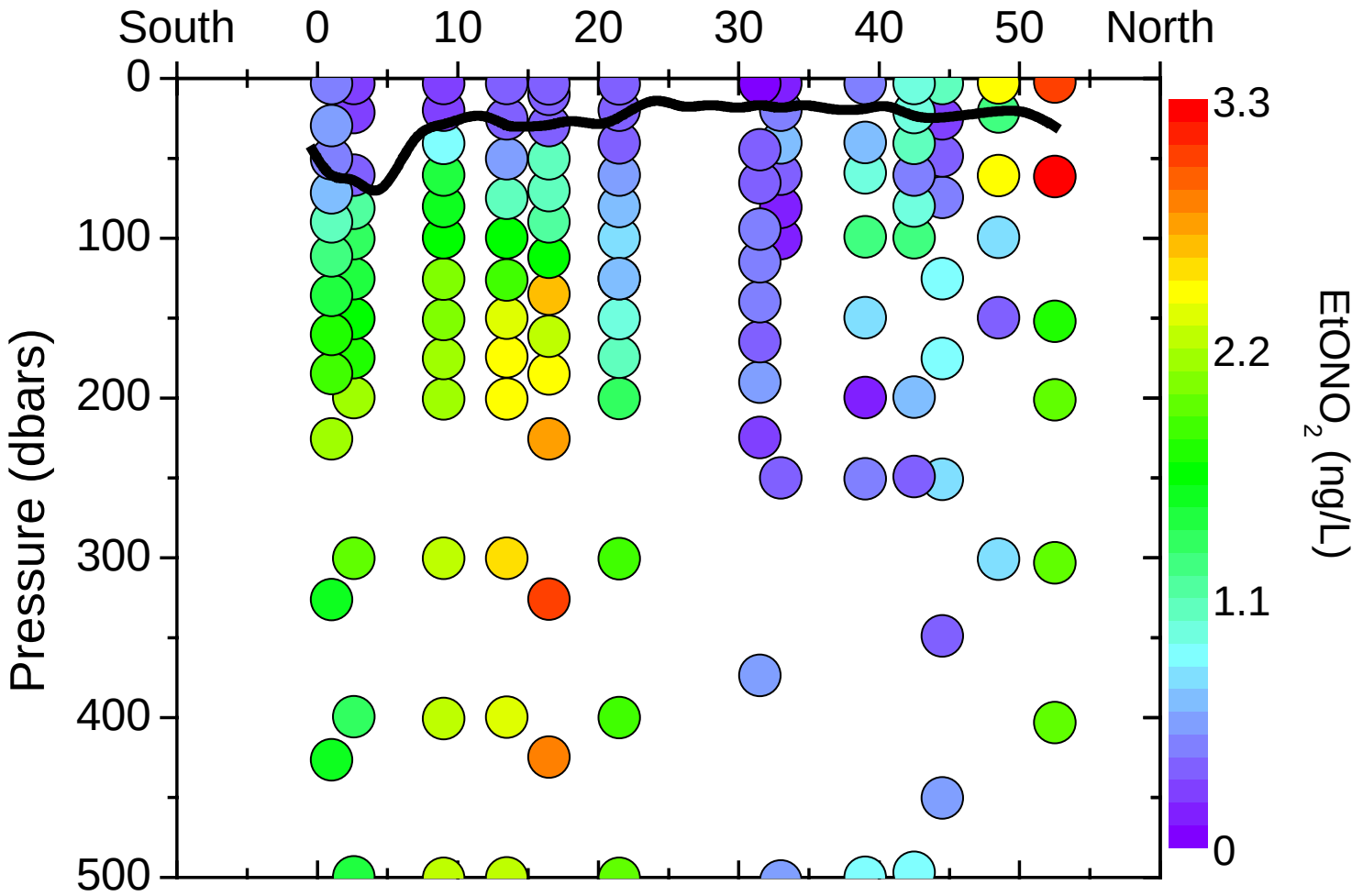

S-26
S-34
S-42
S-46
S-53
S-65
S-68
S-89
S-99
S-105
S-114
S-127
S-132
0.01
0.1
1
10

Depth Profiles

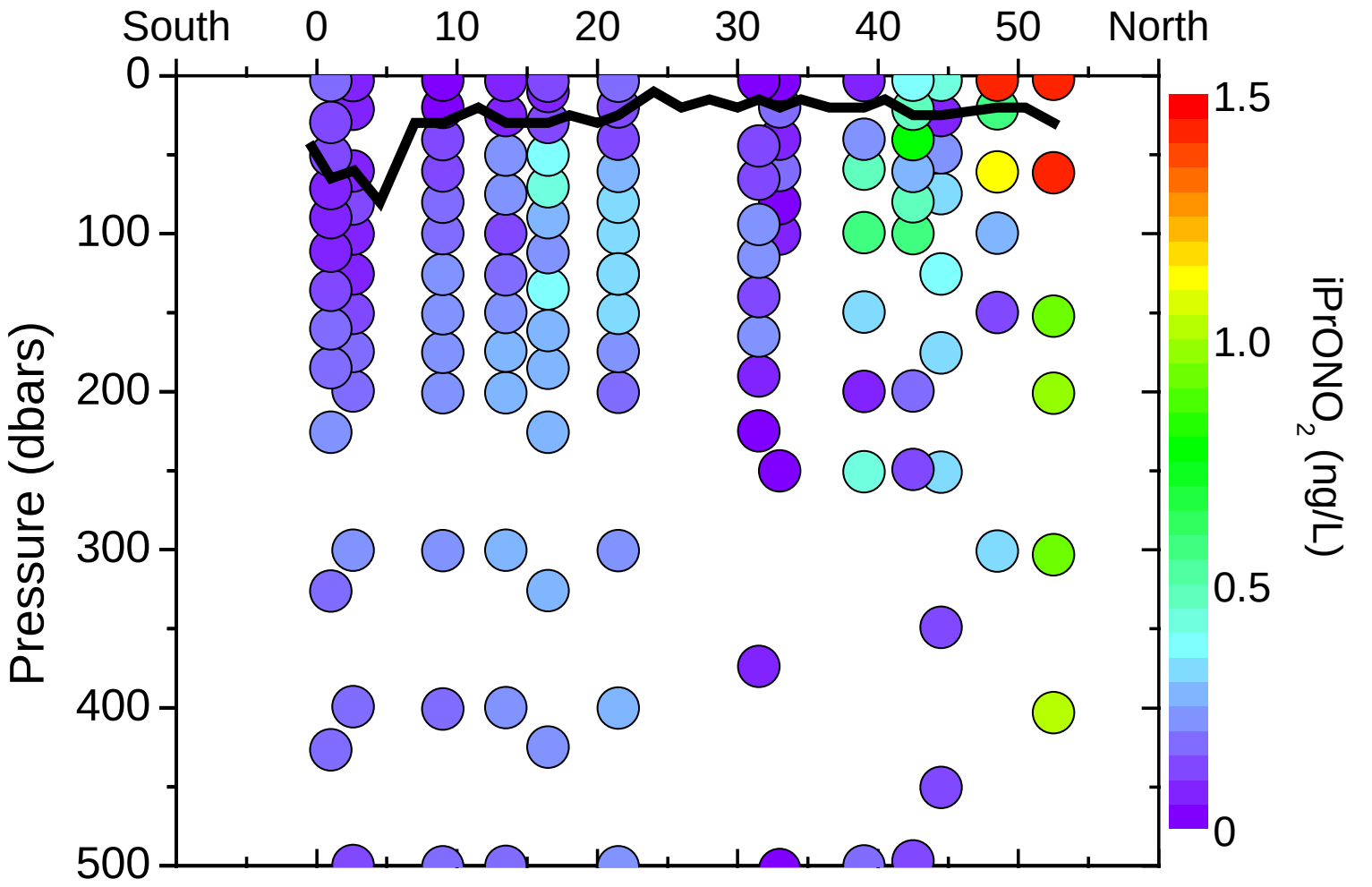
Methyl Nitrate Depth Profiles



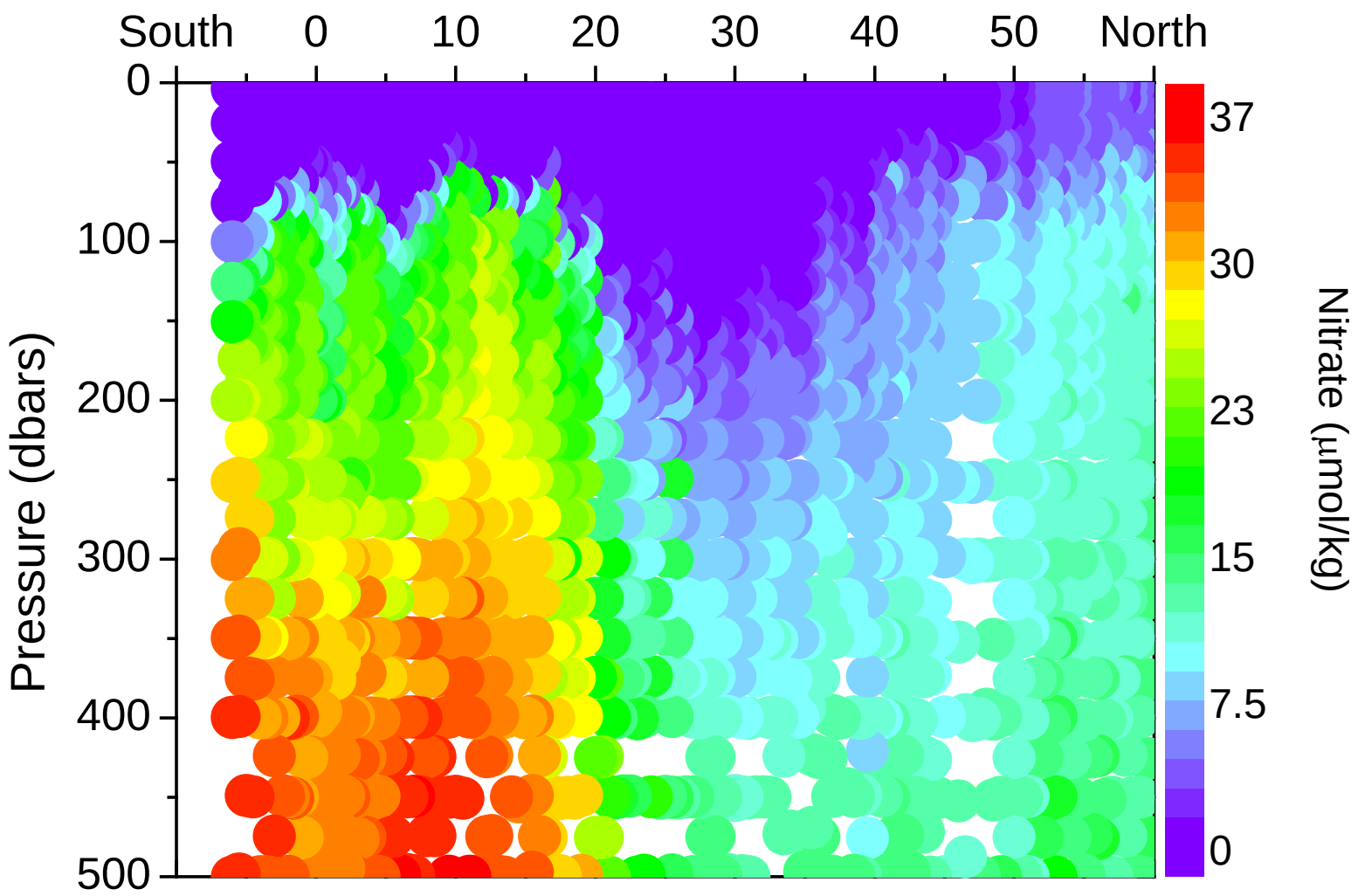
Ethyl Nitrate Depth Profiles



Isopropyl Nitrate Depth Profiles



Nitrate

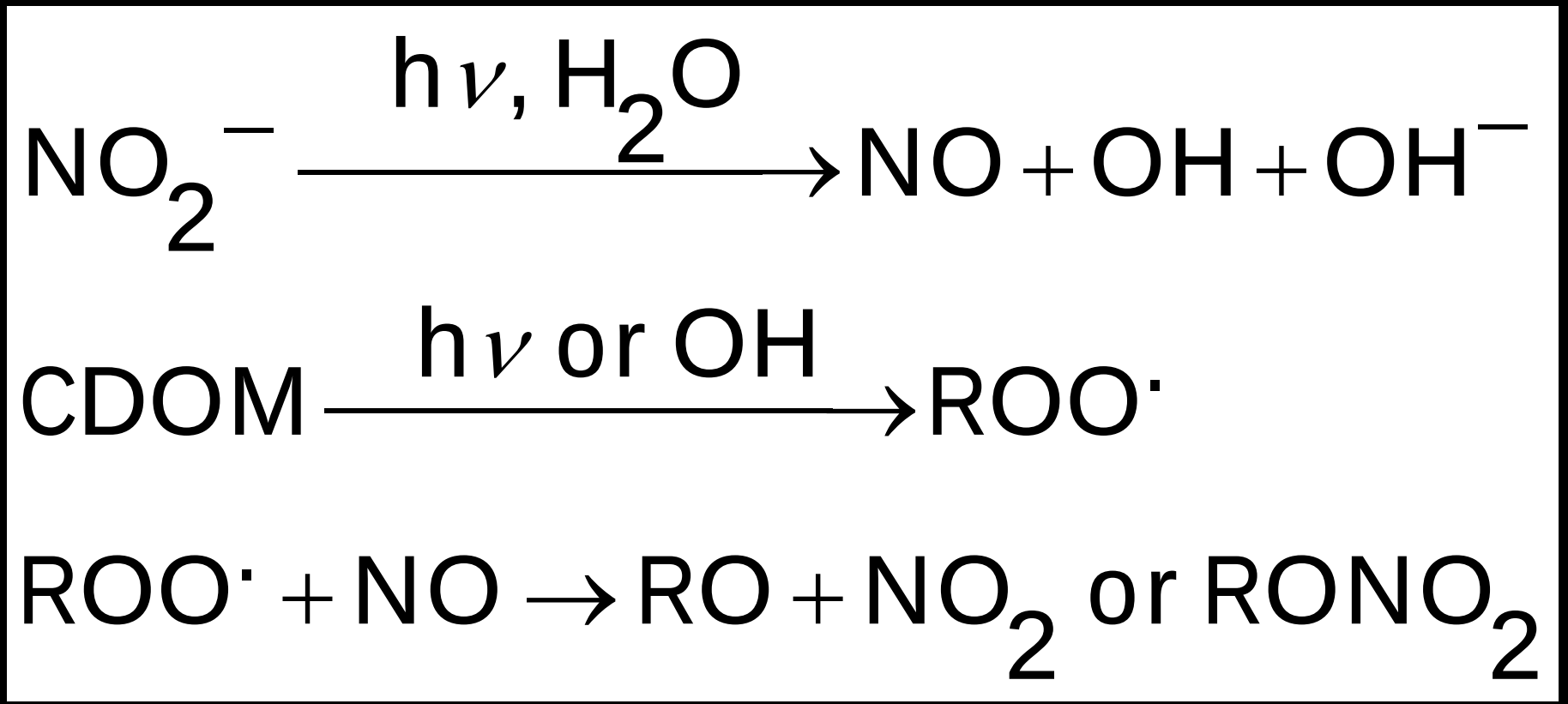

South
0
10
20
30
40
50
North
0
100
200
300
400
500
Pressure (dbars)
37
30
23
15
7.5
0
Nitrate (µmol/kg)

Where do deep ocean alkyl nitrates come from?

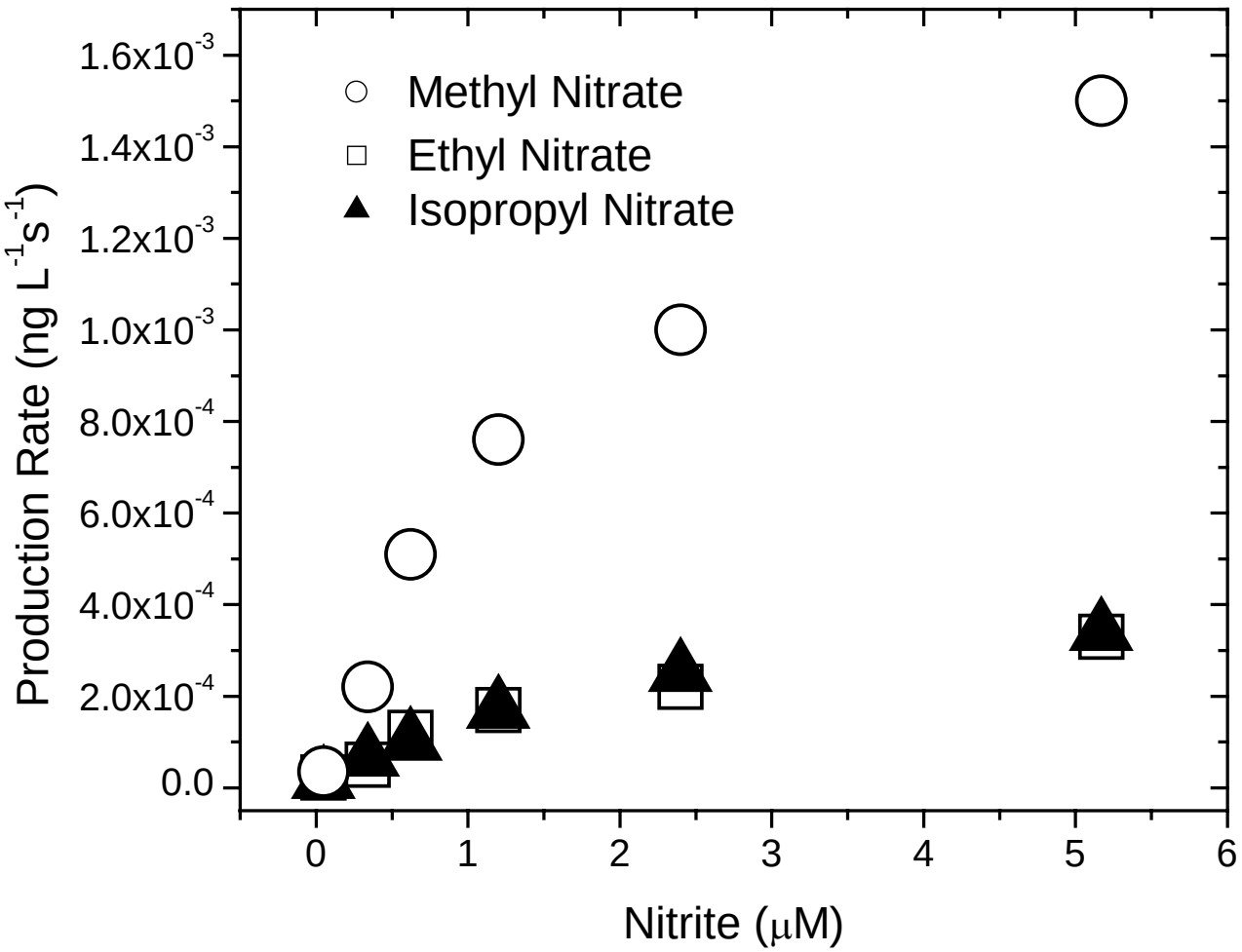
- Bacterial processes?
- Free radical chemistry?
  - Calculated that 0.02 pM/day of OH formed from ^{40}K decay in oceans
  - If every OH formed → $RONO_2$ will produce 10 pM in ~500 days.

Incubation Experiments

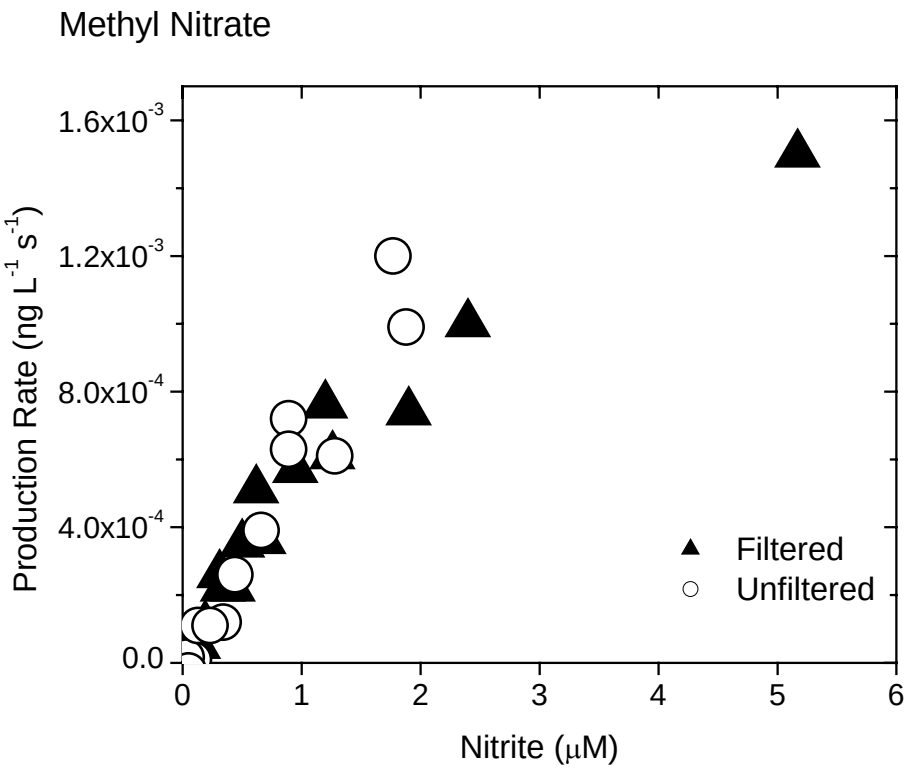
- Collect water from surface
  - Filter to 0.2 μm or
  - Leave unfiltered
- Aliquot water and spike with nitrite.
- Why?

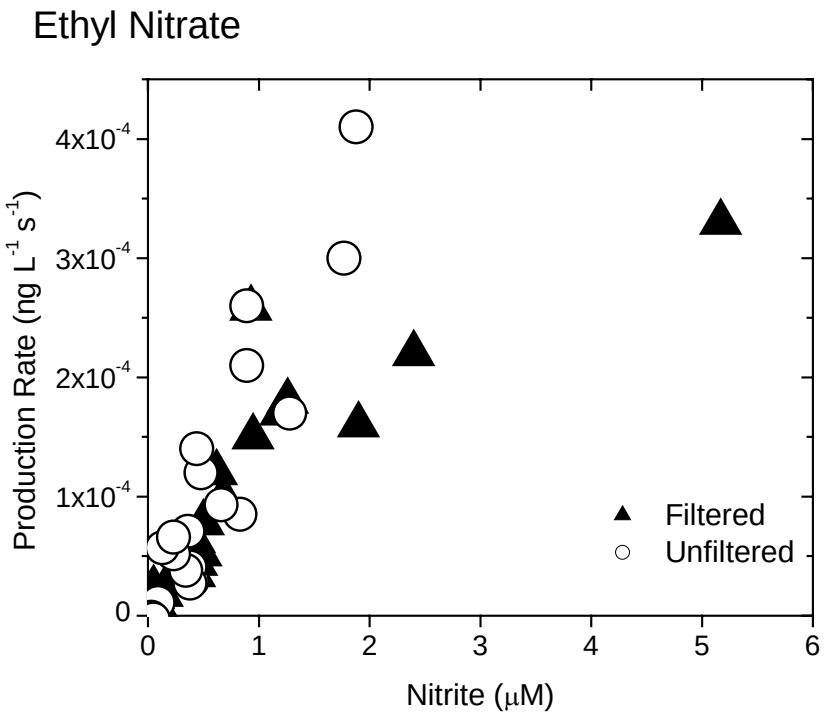

$NO_2^- \xrightarrow{h\nu, H_2O} NO + OH + OH^-$
$CDOM \xrightarrow{h\nu \text{ or } OH} ROO^{\cdot}$
$ROO^{\cdot} + NO \rightarrow RO + NO_2 \text{ or } RONO_2$

Results of One Production Experiment

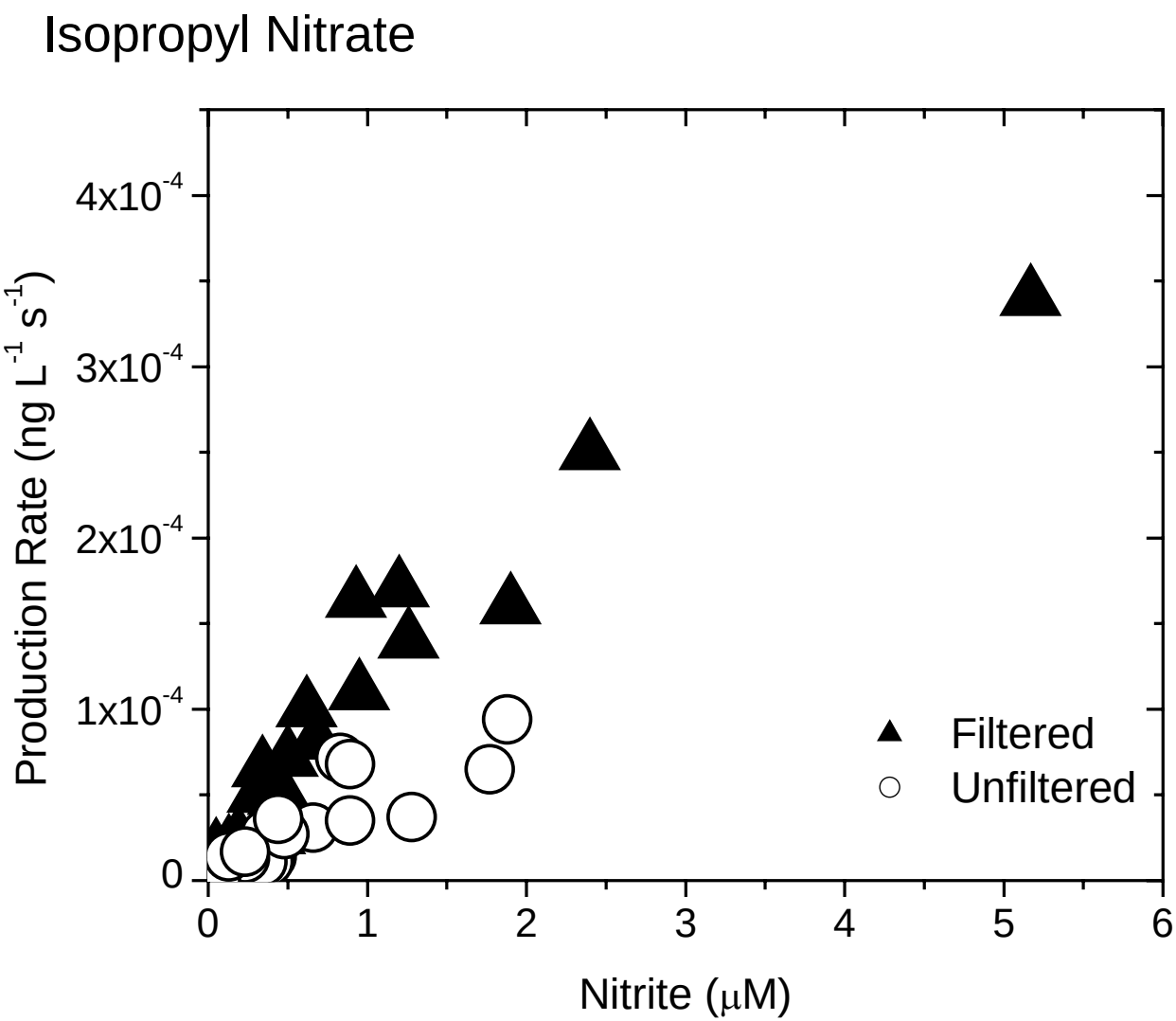


Methyl and Ethyl Nitrate Incubations





Isopropyl Nitrate Incubations



Conclusions

- Surface oceans can be explained by photochemical production.
- Source for deep ocean alkyl nitrates could be free radical chemistry.
- Alkyl nitrate production in natural waters is directly related to nitrite concentration.

Life Lessons

Anything can go wrong no matter how well prepared you are.

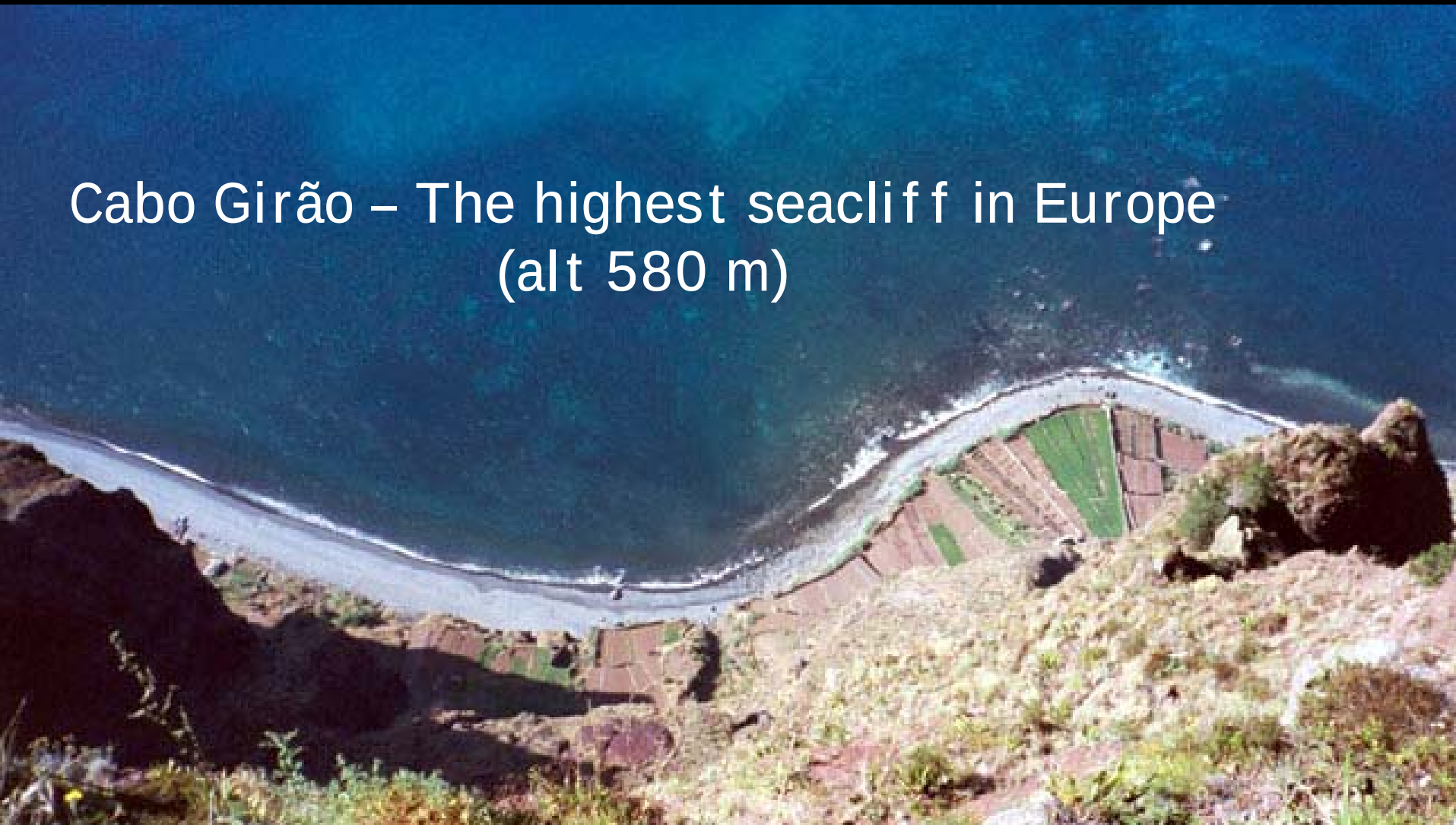
Anything can go wrong no matter how well prepared you are.

- Fortunately…
  - There is usually someone more seasoned than you are.
  - Ship's Engineers
- And…

Always remember there is a light at the end of the tunnel.

In Port – Take advantage of local beverages

Don’t let a little matter of heights stop you from a cool picture.




Stop and smell the flowers.


Get blackmail photos when possible

Acknowledgments

- DOE-GCEP
- John Bullister (NOAA PMEL)
- Eric Saltzman – my advisor
- Shari Yvon-Lewis (formerly of AOML now at Texas A&M)

Temperature